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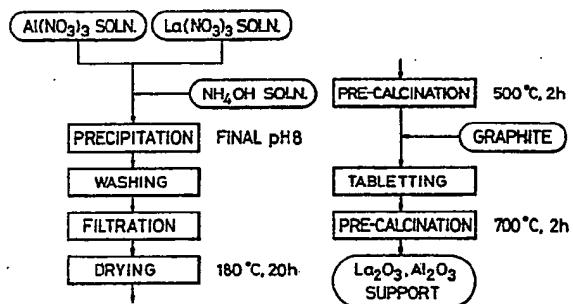
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54 High temperature stable catalyst, process for preparing same and process for conducting chemical reaction using same.

57 The disclosure is concerned with a high temperature stable catalyst comprising an alumina base support and a catalytically active component supported on the support. The support is featured by its specific composite oxide having a specific surface area of at least 10 m²/g and a structural form of amorphous state or a phase resemble to lanthanide β -alumina. The composite oxide can be converted to lanthanide β -alumina when heated to an elevated temperature above 1000°C within 2 hours. The composite oxide is substantially free from such ingredients as accelerate grain growth of alumina. The ingredients are for example Cr, Sr or Ce.

The present disclosure is also concerned with a process for preparing the catalyst and a process for conducting chemical reactions such as steam reforming, desulfurization of heavy oil, cracking of hydrocarbons, etc. using the catalyst.



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High Temperature Stable Catalyst, Process for Preparing
Same, and Process for Conducting Chemical Reaction using Same

Detailed Description of the Invention

5 Field of the Invention

The present invention relates to a high temperature stable catalyst, a process for preparing the same and a catalytic reaction process using the high temperature stable catalyst.

The catalyst used in the present invention is highly active over a very wide range of temperature and particularly stable even at a temperature of 800°C or above.

Background of the Invention

As reactions which are carried out in the presence of a catalyst at a high temperature, there have been known treatment of an organic solvent or deodorization by oxidation, treatment of automobile exhaust gas, high-temperature steam reforming and high-temperature denitration. Recently, catalytic combustion techniques are employed in large-volume boilers, gas turbines and aircraft gas turbines.

In these treatment processes, a reaction temperature of at least 600°C is employed and under some conditions, a temperature of as high as 1400 to 1500°C is employed. Therefore, catalysts having a high thermal stability the activity of which is not seriously damaged at such a high

temperature are demanded.

As high-temperature catalysts, there have been used those comprising a noble metal or a base metal supported on a carrier comprising alumina, silica or silica/alumina; or 5 those comprising a noble metal component supported on a carrier comprising a ceramic material such as zirconia, aluminum titanate or silicon nitride coated with active alumina or the like.

However, these catalysts have defects that when they 10 are heated to a temperature of generally above 800°C, the specific surface area thereof is reduced due to phase transition of the carrier or crystal growth and also the surface area is reduced due to coagulation of the active component to deteriorate the catalytic activity thereof remarkably. 15 The catalysts made of the ceramic material have a defect that the catalytic component cannot be used effectively, since the heat resistance of the coating material is low.

There have been known catalysts wherein carrier materials are made of Al_2O_3 and lanthanides as disclosed in the 20 following U.S. Patents.

- (1) U.S.P. 3,993,572 "Rare Earth and Platinum Group Metal Catalyst Composition"
- (2) U.S.P. 3,966,391 "Method of Combustion using High Temperature Stable Catalysts"
- 25 (3) U.S.P. 3,956,188 "Compositions and Methods for High

Temperature Stable Catalysts"

(4) U.S.P. 3,899,444 "Exhaust Gas Catalyst Support"

(5) U.S.P. 3,867,312 "Exhaust Gas Catalyst Support"

(6) U.S.P. 3,714,071 "Low Density Alumina Spheres of
5 Improved Strength at High Temperature"

(7) U.S.P. 4,056,489 "High Temperature Stable Catalyst
Composition and Method for its
Preparation"

(8) U.S.P. 4,021,185 "Compositions and Methods for High
10 Temperature Stable Catalyst"

(9) U.S.P. 4,220,559 "High Temperature-Stable Catalyst
Composition"

(10) U.S.P. 4,061,594 "Alumina-based Bodies Obtained by
Agglomeration which are resistant to
15 Elevated Temperature"

Other prior art includes U.S.P. No. 3,978,004, U.S.P. No. 3,956,186, U.S.P. No. 3,931,050, U.S.P. No. 3,898,183, U.S.P. No. 3,894,140, U.S.P. No. 3,883,445, U.S.P. No. 3,880,775, U.S.P. No. 3,867,309, U.S.P. No. 3,819,536, 20 U.S.P. No. 4,374,819, U.S.P. No. 4,369,130, U.S.P. No. 4,318,894, U.S.P. No. 4,233,180, U.S.P. No. 4,206,087, U.S.P. No. 4,177,163, U.S.P. No. 4,153,580, U.S.P. No. 25 4,170,573, and U.S.P. No. 4,054,642.

Among the prior art listed above, U.S.P. No. 3,966,391, U.S.P. No. 4,170,573 and U.S.P. No. 4,061,594 seem to be

relevant to the present invention. The U.S.P. '391 discloses a process for producing a catalyst which comprises preparing a solution containing $\text{La}(\text{NO}_3)_3$, CrO_3 and $\text{Sr}(\text{NO}_3)_3$, adding Al_2O_3 powder in the solution, stirring the mixture to impregnate 5 the Al_2O_3 powder with the solution, heating the mixture under stirring to evaporate the liquid, drying the mixture at 110°C , and calcining the dried mixture at 1200°C for 2 hr. The catalysts obtained are used for combustion of carbonaceous fuel.

10 The U.S.P. '573 discloses a process for preparing a catalyst which comprises impregnating Al_2O_3 powder with an $\text{La}(\text{NO}_3)_3$ solution, drying the impregnated Al_2O_3 powder at 160°C for 16 hrs, calcining the dried Al_2O_3 powder at 1250°C for 1 hr, impregnating the calcined Al_2O_3 powder with a 15 $\text{Ce}(\text{NO}_3)_3$ solution, drying the impregnated $\text{La-Ce-Al}_2\text{O}_3$ powder at 160°C for 16 hrs, impregnating the $\text{La-Ce-Al}_2\text{O}_3$ powder with a PtCl_4 solution, and calcining the $\text{Pt-La-Ce-Al}_2\text{O}_3$ powder at 427 to 649°C .

20 The U.S.P. '594 discloses a process for producing a catalyst which comprises autoclaving Al_2O_3 at 600°C , calcining the precipitate at 500°C , impregnating the calcined with a $\text{La}(\text{NO}_3)_3$ solution, drying the impregnated Al_2O_3 , impregnating the dried $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ with a solution of a platinum group element, and calcining the impregnated $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ at 1000°C 25 or 1200°C .

Journal of Solid State Chemistry 19, 193-204 (1976)
discloses structural investigation of the lanthanum β -Alumina
phase, the disclosure of which is not concerned with a catalyst.

5 Summary of the Invention

An object of the present invention is to provide a
catalytic reaction process using a heat-resistant catalyst.

γ - or η -Alumina having a high specific surface area has
been used frequently as a carrier or coating material.

10 However, at a temperature of above 800°C, particularly above
900°C, the specific surface area is reduced due to the phase
transition into α -alumina and increase of the crystal particle
diameter and, consequently, the particles of the noble metal
or base metal used as the catalytically active component are
15 coagulated to deteriorate the catalytic activity.

After intensive investigations made for the purpose of
overcoming the thermal instability of alumina and also pre-
venting the coagulation of the particles of the catalytic
component supported on the carrier, the inventors have found
20 that a catalyst comprising a catalytically active noble metal
or base metal supported on a lanthanum β -alumina ($\text{La}_2\text{O}_3 \cdot 11\text{-}14\text{Al}_2\text{O}_3$),
praseodymium β -alumina ($\text{Pr}_2\text{O}_3 \cdot 11\text{-}14\text{Al}_2\text{O}_3$),
neodymium β -alumina ($\text{Nd}_2\text{O}_3 \cdot 11\text{-}14\text{Al}_2\text{O}_3$); (hereinafter referred
to as L- β -alumina) carrier obtained by adding lanthanum etc. to
25 aluminum is effective.

The present invention provides a heat-resistant catalyst comprising a catalytically active component supported on a support containing a composite oxide of aluminum and lanthanum.

The composite oxide of aluminum and lanthanum is a mixture 5 of lanthanum β -alumina and a precursor that is convertible to lanthanum β -alumina when heated to a temperature of 1000°C for 2 hours, or the composite oxide consists substantially of the precursor.

The high temperature stable catalyst of the present invention 10 for example comprises a support and a catalytically active component supported on said support, wherein at least the part of said support that predominantly supports said active component comprises a composite oxide of aluminium and at least one member selected from the group of lanthanum, neodymium, 15 praseodymium and mixtures thereof, said composite oxide having a specific surface area of at least 10 m^2/g , where said composite oxide contains less than 1% by weight of chromium, strontium and cerium, and is a mixture of L- β -alumina and its precursor that is convertible to L- β -alumina 20 when heated to an elevated temperature above 1000°C within e.g. 10 hours (or even 2 hours) or substantially the precursor.

Brief Description of the Drawings

Fig. 1 is a flow chart showing preparation of La_2O_3 .
25 Al_2O_3 support.

Fig. 2 is a graph showing the relationship between a surface area of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ with various La/Al ratio calcined at 1000, 1200, 1400°C, wherein -○- denotes 1000°C, -●- 1200°C, and -■- 1400°C.

5 Figs. 3a to 3d are X-ray diffraction patterns of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ with various La/Al ratio, wherein calcination was conducted at 1200°C for 2 h. □ denotes $\alpha\text{-Al}_2\text{O}_3$, ○ $\text{La-}\beta\text{-Al}_2\text{O}_3$, and ▲ LaAlO_3 .

10 Fig. 4 is a graph showing the relationship between formation of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ compounds observed X-ray diffraction analysis. □ denotes $\alpha\text{-Al}_2\text{O}_3$, ● $\text{La-}\beta\text{-Al}_2\text{O}_3$, ○ LaAlO_3 , and △ La_2O_3 .

15 Fig. 5 is a graph showing activity of Pd-catalyst supported on $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ for CH_4 oxidation, wherein a gas mixture consisted of CH_4 0.1 % in air, and the catalyst was calcined at 1200°C. □ denotes $\alpha\text{-Al}_2\text{O}_3$, ● La/Al=5/95, ○ La/Al=10/90 and ▲ La/Al=50/50.

20 Fig. 6 is a graph showing the Pd surface area supported on $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$.

Fig. 7 is a graph showing durability of the Pd-catalyst supported on Al_2O_3 and $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ for CH_4 oxidation, wherein a gas mixture consisted of CH_4 3% in air. The inlet temperature was 500°C. □ denotes $\alpha\text{-Al}_2\text{O}_3$ calcined at 1000°C and ● La/Al=5/95 calcined at 1200°C.

Detailed Description of the Invention

The L- β -alumina is a compound represented by the formulae:

$\text{La}_2\text{O}_3 \cdot 11-14\text{Al}_2\text{O}_3$, $\text{Pr}_2\text{O}_3 \cdot 11-14\text{Al}_2\text{O}_3$ or $\text{Nd}_2\text{O}_3 \cdot 11-14\text{Al}_2\text{O}_3$.

These composite oxides may be obtained by heat-treating hydroxides or oxides of Al and La, Nd and/or Pr or by calcining a mixture of starting compounds which yield the oxides by heat treatment at a temperature of 800°C or higher.

Even when the catalyst comprising a catalytically active component supported on the support made of the composite oxides of aluminum and lanthanum, praseodymium and/or neodymium is used at a temperature of as high as 1000°C or above, the catalytically active component is hardly coagulated by heat and its stable catalytic activity can be maintained, since the interaction between the composite oxide of aluminum and lanthanum, etc. and the catalytically active component is strong.

The composite oxide is a mixture of L- β -alumina and its precursor or the composite oxide is made of the precursor.

The composite oxide mentioned above has a high heat resistance and a large specific surface area. Further, it has been made apparent from detailed X-ray diffraction and electron microscopic observation that this compound has an effect of retarding the phase transition from active alumina into alumina and the crystal growth.

It has been made apparent from N_2 adsorption tests that

the reduction of the specific surface area of the support comprising the composite oxide of aluminum and lanthanum (hereinafter the description is made with respect to La for simplicity) at a high temperature is only small. The dispersion state of palladium or platinum (catalytic component) supported on said composite oxide was examined by electron microscopy and carbon monoxide chemical adsorption method to reveal that the good dispersion state was maintained even after the calcination at 1200°C.

10 The composite oxide of aluminum and lanthanum may be applied to a ceramic material to form a coating or the former may be mixed with the latter. For example, the composite oxide may be used in the form of a mixture with a heat-resistant oxide such as α -alumina, titania, zirconia, magnesia, 15 cordierite, mullite or aluminum titanate. Further, the composite oxide may be applied to a material other than the oxides, such as silicon carbide or silicon nitride, to form a coating or the former may be mixed with the latter. In forming the mixture, the amount of the composite oxide of aluminum 20 and lanthanum is controlled preferably to at least 50 % based on the total amount of the support. In case of preparation of the support by coating, a gel or solution of salts of Al and La, Pr and/or Nd which can be prepared by, for example, coprecipitation is coated on a ceramic or metallic support 25 and the coating is dried and calcined to obtain the desired

porous heat-resistant support surface.

The following facts have been confirmed by the present inventors.

(1) Lanthanum, praseodymium and neodymium have exhibited 5 the similar effect on the stabilization of the support at elevated temperature. However, cerium which is one of rare earth metals gave adverse effect on the stabilization. Further, other elements such as chromium, zirconium, strontium, calcium, sodium showed acceleration of sintering or grain 10 growth of alumina when the Al_2O_3 support containing Cr, Sr, Ca, Na is calcined at 1200°C or higher. This phenomena results in the reduction of the surface area of the support.

(2) The composite oxide should have a specific surface area of at least $10 \text{ m}^2/\text{g}$, and be in the form of an amorphous state, 15 or a structure resembling to L- β -alumina or a precursor which can be converted to L- β -alumina when heated to 1400°C for 2 hours. The composite oxide should desirably be in the structural form other than α -, γ -, θ -, η -, κ -, χ -, ρ - or δ -form. The surface area of the composite oxide should preferably be of 20 to 20 $100 \text{ m}^2/\text{g}$.

(3) The amounts of L- β - Al_2O_3 in the composite oxide are preferably in the range of from about 15 to about 95% by weight. When the molar ratio of La_2O_3 to Al_2O_3 in the starting material (i.e. before calcination) is 1 to 99, the amount of L- β - Al_2O_3 is 25 about 15% by weight. When the molar ratio of La_2O_3 to Al_2O_3

is 20 to 80, the amount of L- β -Al₂O₃ is about 95% by weight. Similarly, at the molar ratio of La₂O₃ to Al₂O₃ being 10 to 90, the amount is about 90% by weight, at the ratio of La₂O₃ to Al₂O₃ being 5 to 95, the amount is about 64, and at the molar 5. ratio of La₂O₃ to Al₂O₃ being 2 to 98, the amount of L- β -Al₂O₃ is about 27% by weight.

The amount of the mixture of L- β -Al₂O₃ and its precursor or the precursor in the composite oxide should be predominant or at least 50% by weight.

10 L- β -Al₂O₃ has characteristic peaks at degrees of 18.9⁽⁷⁾, 20.1⁽⁹⁾, 32.3⁽⁵⁾, 34.0⁽²⁾, 36.2⁽¹⁾, 39.4⁽⁸⁾, 40.9⁽¹⁰⁾, 42.8⁽⁴⁾, 45.1⁽⁶⁾, 58.0⁽¹¹⁾ and 67.4⁽³⁾ in terms of Bragg angles (2θ) of X-ray diffraction pattern. The circled numbers represent the order of the strengths of peaks. The composite oxide calcined 15 at 1200°C showed characteristic peaks at 18.9°, 20.1°, 32.3°, 34.0°, 36.2°, 42.8°, 45.1°, 58.0° and 67.4°; this fact means that the composite oxide contains L- β -Al₂O₃ (see Figs. 3b to 3c).

20 Since the diffraction patterns shown in Figs. 3b and 3c are somewhat broadened, compared to those of crystal forms (Figs. 3a and 3d), the composite oxide comprises L- β -Al₂O₃ and the precursor which may be a form other than α -, γ -, θ -, η -, κ -, δ -, χ - or ρ -form, but the precursor should be amorphous. In Figs. 3b and 3c there are marked by black 25 dots peaks at 32.3°, 36.2°, 42.8°, 45.1° and 67.4°.

(4) When an alumina support of such as α -, γ -, β -, δ -, ϵ -, κ -, γ - or σ -form is impregnated with a solution of lanthanum, praseodymium and/or neodymium salt and calcined at a temperature of 1000 to 1200°C for 2 hours, an appreciable amount of L- δ -alumina is not produced on or in the surface of the support.

The high temperature stable catalyst according to the invention may employ a support which is wholly made of the composite oxide.

10 The high temperature stable catalyst according to the invention can have the shape of a honeycomb structure.

The high temperature stable catalyst according to the invention may comprise the part for supporting the active component and a substrate for carrying the support.

15 The substrate can be made of a member selected from a metallic plate, metallic mesh, and foamed metal.

The high temperature stable catalyst according to the invention can have a surface of the support coated with the composite oxide on which said active component is supported.

20 A process which is preferentially employed for preparing a high temperature stable catalyst comprises effecting co-precipitation of an aluminum salt and a salt of lanthanum, praseodymium and or neodymium from an aqueous solution of the salts by adding an alkali to the solution;

25 separating the resulting precipitate;

shaping the precipitate; and
heating to a temperature higher than 1000°C the shaped
precipitate to convert it into a composite oxide of aluminium
and lanthanum, neodymium and/or praseodymium, whereby said
5 composite oxide has a specific surface area of at least 10 m²/g,
and a structural form other than α -, γ -, θ -, η -, κ -, χ -, ρ -
and δ - forms is a precursor convertible to L- β -alumina when
heated to a temperature above 1000°C within 2 hours or a
mixture of L- β -alumina and the precursor.

10 Further, the catalyst support for the present invention
may be prepared by homogeneously mixing fine powders of oxides
or salts of aluminium and lanthanum, neodymium and/or praseo-
dymium in the dry state or wet state, shaping the mixture,
and calcining the mixture at a temperature of 800°C or above,
15 preferably at 1000°C or above to produce the desired precursor
or the mixture.

If the calcination temperature for preparing the support
is lower than 800°C, the precursor can not be appreciably
converted to L- β -alumina when heated to a temperature above
20 1000°C within 2 hours.

The support of the invention can be prepared by the
following manners:

(1) A starting material of the composite oxide, i.e. a homo-
geneous mixture of salts of Al and La, is preliminarily
25 calcined at a temperature of, for example, 800°C or below.

Then the resulting precursor of the composite oxide is calcined at a temperature of 900°C or higher for a predetermined period of time so that the precursor is converted to a desired mixture of L- β -alumina and its precursor or the precursor that is convertible to L- β -alumina when heated to a temperature above 1000°C within 10 hours.

(2) The starting material of the composite oxide is preliminarily calcined at a temperature of, for example, 800°C or below. Then, the resulting precursor of the composite oxide is impregnated with a solution of a catalytically active component or is coated with the catalytically active component to support the component on the precursor of the composite oxide. The resulting product is then calcined at a temperature of 900° to 1500°C for a predetermined period of time to convert the precursor to another form of composite oxide, i.e. a mixture of L- β -alumina and the precursor of L- β -alumina.

The calcination temperature for forming the desired composite oxide of Al and La is above 900°C, preferably 1000°C. If a calcination temperature is lower than 900°C, the desired composite oxide can not be obtained with a practical period of time.

The structural feature of the composite oxide of the present invention may be amorphous or a structure resembling L- β -alumina. The structure is dependent on the calcining

conditions, particularly temperature and time periods. The higher the temperature for calcining, the higher the degree of conversion of the structure of the composite oxide to the L- β -alumina becomes.

5 When the precursor of the composite oxide is calcined at 1500°C for 1 hour or longer, the crystal growth of the composite oxide is too much, resulting in reduction of the specific surface area.

Even when the calcining temperature is 900°C, the desired 10 composite oxide may be obtained when the calcining is conducted at 900°C for 100 hours or longer.

The calcining conditions are chosen from the practical point of view. Preferable calcining conditions are in the range of from 1000°C \times at least 1 hours to 1400°C \times 0.5 hours or less.

15 The pressure for calcination does not have signification.

The most preferable calcining conditions are in the range of from 1100°C \times 1 to 10 hours to 1300°C \times 0.5 to 2 hours under a pressure of 100 kg/cm² or less.

A powder containing the composite oxide may be shaped 20 into in various forms such as globules, cylinders, rings and honeycombs. A slurry of the powder containing the composite oxide may be applied to a metallic substrate such as metallic plate, mesh, foamed metal, or to an inorganic heat-resistant support such as ceramic material, for example, 25 mullite, cordierite, α -alumina, zircon, aluminum titanate,

silicon carbide or silicon nitride in various shapes to form a coating. The amount of the composite oxide to be supported on the inorganic heat-resistant support is at least 5 %, preferably 5 to 30 %, based on the total weight of the support.

5 The composite oxide of aluminum and lanthanum may be prepared by, for example, an ordinary precipitation method, deposition method, kneading method or impregnation method.

Among the methods mentioned above, a coprecipitation method is most suitable for producing a highly homogeneous 10 complex oxide. Moreover, the coprecipitation method is most effective to produce L- β -alumina or its specific precursor.

The composite oxide may be prepared by coprecipitation or a method wherein alumina and/or alumina sol are mixed 15 intimately with lanthanum oxide and/or lanthanum hydroxide and the resulting mixture is calcined; or a method wherein alumina is impregnated with a lanthanum salt solution and then calcined by heating.

It is preferred to coprecipitate an intimate mixture of 20 aluminum and lanthanum by adding an alkali to an aqueous solution containing aluminum and lanthanum prior to the calcination, since the intended composite oxide of aluminum and lanthanum can be obtained even at a relatively low calcination temperature.

25 Starting materials for aluminum usable in the present

invention include soluble salts such as nitrate, sulfate and chloride; organic salts such as alkoxides; hydroxide; and oxide thereof. Starting materials for lanthanum, neodymium and praseodymium usable in the present invention include 5 soluble salts such as nitrate, chloride and oxalate; hydroxide; and oxide thereof.

A rare earth mixture containing lanthanum, neodymium and/or praseodymium but substantially free from cerium may also be used.

10 The catalytically active component is supported on the support finally in the form of the metal or its oxide.

The catalytically active component may be supported on the carrier by an ordinary method such as impregnation or kneading. Starting materials for the catalytically active 15 components include inorganic salts and complex salts.

The catalyst of the present invention is usable for combustion reactions of fuels such as hydrogen, carbon monoxide, hydrocarbons or alcohols, deodorization, denitration reaction, high-temperature steam reforming reaction and 20 cleaning of automobile exhaust gas.

When the catalyst of the present invention is used for the combustion reaction of at least one combustible component selected from the group consisting of hydrogen, carbon monoxide, alcohols and hydrocarbons, it is desirable to use a Group VIII element 25 of the Periodic Table, manganese, chromium, zirconium, rare

earth element, tin, zinc, copper, magnesium, barium, strontium or calcium as the catalytically active component. The fuels to be subjected to the combustion reaction include, for example, methane, ethane, propane, butane, kerosene, diesel 5 oil, light oil, etc.. The reaction temperature which varies depending on the kind of the fuels ranges broadly from room temperature to 1500°C. In the combustion reaction, said gas is contacted with the catalyst in the presence of an oxygen-containing gas. When methane is used as the fuel, a reaction 10 temperature in the range of 400 to 1500°C is particularly preferred and a platinum group metal is used preferably as the catalytically active component.

When the catalyst of the present invention is used for cleaning an exhaust gas from an internal combustion engine 15 of, for example, an automobile, there is used at least one catalytically active component selected from the group consisting of Group VIII elements of the Periodic Table, manganese, chromium, zirconium, rare earth elements, tin, zinc, copper, magnesium, barium, strontium and calcium and 20 the exhaust gas and oxygen are contacted with the catalyst at a reaction temperature of 150 to 1500°C. It is particularly preferred to use a Group VIII metal of the Periodic Table as the catalytically active component.

By this treatment, carbon monoxide and hydrocarbons 25 contained in the exhaust gas can be oxidized and nitrogen

oxides can be converted into harmless nitrogen and water.

When the catalyst of the present invention is used for the steam reforming of hydrocarbons, at least one member selected from the group consisting of Group VIII elements of the Periodic Table, alkali metals and alkaline earth metals is used as the catalytically active component and the reaction is carried out in the temperature range of 400 to 1000°C to form a gas comprising hydrogen and carbon monoxide. It is preferred to use the Group VIII elements of the Periodic Table, particularly nickel or a mixture of nickel and cobalt as the catalytically active component.

When the catalyst of the present invention is used for the reduction of nitrogen oxides contained in an exhaust gas from a boiler or a gas turbine, the reaction is carried out using ammonia as a reducing agent at a temperature of 400 to 1500°C. It is preferred to use at least one member selected from the group consisting of Group VIII elements of the Periodic Table, alkaline earth metals, titanium, zirconium, vanadium, rare earth elements, Groups Va and VIa elements of the Periodic Table, manganese, zinc, aluminum and tin as the catalytically active component(s).

They are supported on the carrier finally in the form of their oxides. Particularly preferred catalytically active component is at least one of tungsten, vanadium, titanium, tin, cerium, iron, nickel and/or cobalt.

When the catalyst of the present invention is used for the methanation, it is preferred to use at least one member selected from the group consisting of Group VIII elements of the Periodic Table, zinc, chromium, molybdenum, tin, vanadium and cerium as the catalytically active component and a carbon monoxide-containing gas and hydrogen are contacted with the catalyst at a temperature of 250 to 800°C. Preferred catalytically active component is a Group VIII metal of the Periodic Table, particularly nickel.

When the catalyst of the present invention is used for the dehydrogenation reaction of hydrocarbons, at least one catalytically active component selected from the group consisting of chromium, zinc, vanadium, copper, silver, iron, nickel and cobalt is used and the hydrocarbons are contacted with the catalyst at a temperature in the range of room temperature to 1500°C. It is desirable to use at least one of copper and zinc as the catalytically active component. The reaction temperature is preferably 300 to 1000°C.

20

Preparatory Example

Preparation of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ Supports

A procedure for preparation of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ supports is

shown in Fig. 1. A mixed solution of $\text{La}(\text{NO}_3)_3$ and $\text{Al}(\text{NO}_3)_3$ was neutralized by addition of an NH_4OH solution and the precipitate was washed thoroughly and dried. After preliminary calcining at 500°C , the powder with 1 wt% graphite was 5 tabletted into a columnar shape of 3 mm diameter and 3 mm height. A support consisting of La_2O_3 and Al_2O_3 was obtained by preliminary calcining the tablets at 700°C for 2 hours. For comparisons a support consisting only of Al_2O_3 or La_2O_3 was also prepared by the same procedure. A mixed oxide 10 consisting of 5 mol% La_2O_3 and 95 mol% Al_2O_3 is denoted as $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (5/95) in the following part of this paper. To give an example, a BET surface area of $130 \text{ m}^2/\text{g}$ and porosity of 0.40 ml/g (measured by water pick-up) were obtained for $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (5/95) support.

15. Preparation of Pd Catalyst

The support was impregnated in a $\text{Pd}(\text{NO}_3)_2$ solution, the Pd loading in the final catalyst being 1 wt%. The Pd catalysts supported on the $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ supports were preliminary calcined at 500°C for 30 min. and subsequently at 1200°C for 20 2 hours.

Experimental Apparatus

The activity of catalyst on the CH_4 oxidation was measured using a flow type reactor made of quartz with 18 mm inner diameter. A reaction gas mixture containing 0.1 vol% 25 CH_4 in air was used to measure the activity under isothermal

condition. A gas mixture containing 3 vol% CH_4 in air was used in a durability test which was performed at the inlet temperature of 500°C and the catalyst bed temperature about 1150°C (adiabatic flame temperature $> 1200^\circ\text{C}$). The volume 5 of catalyst was 8 ml and the gas flow rate 240 1/h (at STP), making a space velocity of 30,000 vol/vol/h.

The conversion of CH_4 oxidation was determined by measuring gaseous composition with a gas chromatograph. The crystallographic structure of the supports was investigated 10 by an X-ray diffractometer (Rigaku Denki, RAD- γ A), X-ray microanalyser and transmission electron micrograph (Hitachi HV-11DS). The valence state of Pd on the supports was examined by XPS (Kratos XSAM-800). Specific surface area was measured by the standard BET method, and the Pd metal surface 15 area by the CO adsorption method.

Surface Area and Crystal Structure of $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$

The $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ supports with La content of 0, 2, 5, 10, 20, 20, 50, 75, and 100 mol% were prepared and preliminary calcined at 700°C . The supports were treated in air at 1000 (curve 11), 1200 (curve 12), and 1400°C (curve 13) for 2 hours. Changes of specific surface area are shown in Fig.2. It is clearly shown that the surface area has a maximum between 2 and 5 mol% La. For the supports calcined at 1200°C , 25

the surface area was 33 and 37 m^2/g for $\text{La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ (2/98) and (5/95), respectively, whereas the surface area of Al_2O_3 was 5.6 m^2/g . The surface area decreased gradually as the La content increased from 10 to 100 mol%. Thus, it has been 5 found that the addition of only small amounts of La_2O_3 into Al_2O_3 markedly increases the thermal stability.

The crystal structure of the $\text{La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ supports was examined by X-ray diffraction analysis. Figs. 3a to 3d show a few diffraction patterns obtained for the supports calcined 10 at 1200°C for 2 hrs. Peaks ascribed to $\alpha\text{-Al}_2\text{O}_3$ are observed in the Al_2O_3 support, 4 peaks ascribed to lanthanum- $\beta\text{-Al}_2\text{O}_3$ ($\text{La}_2\text{O}_3\text{-11Al}_2\text{O}_3$) in the $\text{La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ (5/95), and LaAlO in the $\text{La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ (50/50). It is seen that the peaks assigned to lanthanum- $\beta\text{-Al}_2\text{O}_3$ are rather weak and broad, indicating that 15 crystal growth has proceeded only to a small extent. Therefore, the composite oxide obtained is considered as a precursor of lanthanum- β -alumina or a substance resembling to lanthanum- β -alumina.

When the calcining is conducted at 1000°C for 2 hours, 20 the resulting composite oxide showed no appreciable peaks like an amorphous structure. This is considered as a precursor of lanthanum- β -alumina. The above mentioned precursors could be converted to lanthanum- β -alumina by heating at 1400°C for 2 hours. Lanthanum aluminate (LaAlO_3) which has a 25 perovskite structure gives sharp peaks. In the $\text{La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$,

(10/90) the formation of both lanthanum- β -Al₂O₃ and LaAlO₃ is observed.

The formation of various La₂O₃·Al₂O₃ compounds observed by X-ray diffraction analysis between 800 and 1400°C is summarized in Fig. 4. Lanthanum- β -Al₂O₃ or a product resembling it is observed in the supports containing 2 - 30 mol% La, when calcined at 1400°C. LaAlO₃ is readily formed at the lower temperature. It is mentioned that the Al₂O₃ support calcined at 1200°C gives very sharp peaks from α -Al₂O₃, while the La₂O₃·Al₂O₃ (2/98) gives very weak peaks from θ and κ -Al₂O₃. The results indicate that the incorporation of small amounts of La₂O₃ into Al₂O₃ greatly retards the formation and the crystal growth of α -Al₂O₃.

It is reported that La- β -Al₂O₃ is formed via LaAlO₃ at the temperature higher than 1400°C by firing a La₂O₃·Al₂O₃ (8.3/91.7) mixture for 24 hrs "R.C. Ropp and B. Carroll, J. Am. Cer. Soc. 63, 416 (1980)". The formation of La- β -Al₂O₃ at the lower temperature, i.e. 1000°C for 2 hours, in the present invention may result from the difference in the preparation method, i.e., the coprecipitation in the present invention and the mixing of two oxides. The coprecipitation method will give a better mixing of the two oxides.

Observation of the La₂O₃·Al₂O₃ supports by TEM was performed to investigate the particle size. Two typical electron micrographs were obtained as to (A) Al₂O₃ only, and

(B) $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (5/95). It has been found that $\alpha\text{-Al}_2\text{O}_3$ has grown up to a particle size of 500-1500 Å, whereas the $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ has a particle size of 100 - 300 Å. The $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (50/50), i.e. LaAlO_3 , showed a crystal growth to about 5 1000 Å. It is reported in the literature "H. Schaper, et al, Applied Catalysis 7, 211 (1983)" that La_2O_3 decreases the sintering of $\gamma\text{-Al}_2\text{O}_3$ by the formation of LaAlO_3 at the surface layer. The present investigation, however, shows that the retardation of the sintering may be caused by the formation 10 of lanthanum- $\beta\text{-Al}_2\text{O}_3$, not by LaAlO_3 . The discrepancy may be attributed to difference of the preparation method, i.e. $\gamma\text{-Al}_2\text{O}_3$ tablets were impregnated in a $\text{La}(\text{NO}_3)_3$ solution in the literature. Since the concentration of La_2O_3 would be high 15 at the surface layer in the impregnation method, the formation of LaAlO_3 is quite possible.

Activity of $\text{Pd-La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ Catalysts

Activities of the Pd catalysts on the oxidation of CH_4 were measured in a temperature range of 250 and 700 °C using a gas mixture containing 0.1 % CH_4 in air. Under these 20 conditions the reaction is carried out essentially isothermally. Figure 5 shows the activity of the Pd catalysts supported on $\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ with various La/Al ratios. The highest activity was obtained in the $\text{Pd-La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (5/95) as shown by curve 2, while the $\text{Pd-Al}_2\text{O}_3$ showed a poor activity. The activity of 25 $\text{Pd-La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$ (2/98) shown by curve 24 was nearly equal to

that of (10/90) shown by curve 23. It is noted that the Pd-La₂O₃·Al₂O₃ (50/50) shown by curve 22 showed a considerably high activity despite its low surface area of the support (see Fig.2).

5 A measurement of the Pd metal surface area was performed using the CO adsorption method in order to investigate the dispersion of Pd on the supports. The CO uptake at 200°C was measured after treating catalysts in He stream at 250°C. Figure 6 shows the Pd surface area of the catalysts as a
10 function of La content. It is seen that the Pd surface area increases up to La content of 5 - 10 mol%, and then decreases to almost zero at 50 mol%.

Observation of the Pd catalysts by TEM was carried out to investigate Pd particle size on the supports. We obtained
15 two electron micrographs, (A) Pd-Al₂O₃ calcined at 1000°C, and (B) Pd-La₂O₃·Al₂O₃ (5/95) calcined at 1200°C. Since the Pd particles were not always clearly identified on the micrographs, XMA was used to identify the locations of Pd particles. Palladium particles are indicated by arrows as identified by
20 XMA. It was seen that the size of Pd particles is about 1500 - 2000 Å on Al₂O₃, and 300 - 800 Å on La₂O₃·Al₂O₃ (5/95). It may be said that Pd particles coagulate and sinter, as the crystal growth of the supporting Al₂O₃ proceeds. This is so called an "earthquake" effect.
25 Durability of Pd Catalyst Supported on La-β-Al₂O₃

Durability of the Pd combustion catalysts was tested using a gas mixture containing 3 vol% CH₄ at the inlet temperature of 500°C and the catalyst bed temperature of about 1150°C after CH₄ combustion. The test was carried out 5 for 100 hours in the presence of two catalysts in parallel, one with Pd-La₂O₃·Al₂O₃ (5/95) and the other with Pd-Al₂O₃. The latter catalyst was calcined at 1000°C instead of 1200°C, because the catalyst calcined at 1200°C did not ignite the gas mixture at the inlet temperature of 500°C. The result is 10 shown in Fig. 7. The CH₄ conversion was maintained above 99.5% for the Pd-La₂O₃·Al₂O₃ (5/95) shown by curve 32, while it decreased from 99.5 to lower than 98% for the Pd-Al₂O₃ as 15 shown by curve 31.

Table 1

15

	Pd-Al ₂ O ₃		Pd-La ₂ O ₃ ·Al ₂ O ₃ (5/95)	
	Fresh	After 100h	Fresh	After 100h
BET surface area (m ² /g)	62	5.6	36	23.5
Pd surface area (m ² /g-Pd)	42	13.6	58.5	37

20

After the durability test the catalysts were examined by several methods. The BET surface area and the Pd metal surface area are summarized in Table 1. A drastic decrease 25 in the surface areas is observed for Pd-Al₂O₃, and the change

is relatively small for $\text{Pd-La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ (5/95). The activity of the two catalysts after the durability test was measured in a temperature range of 300 and 700°C using the gas mixture containing 0.1 vol% CH_4 under isothermal condition. It was 5 found that the rate constant was reduced by 15 - 20 % relative to the initial value for the $\text{Pd-La}_2\text{O}_3\cdot\text{Al}_2\text{O}_3$ (5/95) and 50 - 80 % for the $\text{Pd-Al}_2\text{O}_3$. The TEM observation showed the existence of Pd particles as large as 3000 - 5000 Å in the $\text{Pd-Al}_2\text{O}_3$ after the test.

10 The following examples will further illustrate the present invention, which by no means limit the scope of the protection of the present invention.

Example 1

375.1 g of aluminum nitrate and 228 g of lanthanum 15 nitrate were dissolved in 1 l of distilled water (Al/La atomic ratio: 95/5). 3 N aqueous ammonia was added dropwise to the solution under stirring to neutralize the same to pH 7.5. The resulting coprecipitate of aluminum salt and lanthanum salt was washed thoroughly with water, dried, 20 pulverized and calcined at 1000°C for 5 h. The resulting powder was shaped into cylinders having 3 mm diameter and 3 mm length by means of a press molding machine.

Separately, a comparative support comprising only alumina was prepared in the same manner as above except that no 25 lanthanum nitrate was used.

Each of the two carriers obtained as above was impregnated with 1 wt. % (as palladium) of a palladium nitrate solution, dried at 120°C for about 5 h and then calcined at 1200°C for 3 h to obtain catalysts of Example 1 and Comparative Example

5 1. The effects of them in the methane combustion reaction were
examined. A continuous test was carried out for 1000 hours
while a gas of the following composition was introduced at a
space velocity of $25,000 \text{ h}^{-1}$.

Gas composition:

10 methane 3 %
 air the balance

In this experiment, the reaction gas was preheated to 500°C. When the methane conversion has reached 90% or higher, the temperature of the catalyst bed is elevated to about 15 1200°C. The durability of the catalyst at high temperature can be evaluated from this fact. The results of the experiment are shown in Table 2.

It is apparent from Table 2 that the catalyst obtained in Example 1 is suitable for use in the catalytic combustion reaction at high temperature.

Table 2

	<u>Catalyst</u>	<u>Methane conversion (%)</u>			
		<u>Test time (h)</u>			
		<u>1</u>	<u>50</u>	<u>100</u>	<u>1000</u>
25	Catalyst of Example 1	>99.9	>99.9	>99.9	>99.5
	Catalyst of Comparative Example 1	99.5	99.4	97.5	96

After the experiment for examining the activities of the catalysts of Example 1 and Comparative Example 1 effected for 100 h, the specific surface areas of them were about $13.6 \text{ m}^2/\text{g}$ and $5.6 \text{ m}^2/\text{g}$, respectively. The surface areas of palladium dispersed on the carrier were $37 \text{ m}^2/\text{g-Pd}$ and $20 \text{ m}^2/\text{g-Pd}$, respectively. Thus, it will be understood that as compared with the catalyst of Comparative Example 1, the catalyst of Example 1 had a larger specific surface area and more excellent Pd dispersion states so that the latter is an excellent heat-
resistant catalyst.

Example 2

3750 g of aluminum nitrate and 480 g of lanthanum nitrate were dissolved in 10 l of distilled water. Then, the same procedure as in Example 1 was repeated to obtain a powder calcined at 1100°C for 3 hours. 2.5 l of distilled water was added to 1 kg of the powder and the mixture was finely divided by means of an oscillating mill until an average particle diameter of the powder had been reduced to about 1 μm to obtain an impregnation liquid in the form of a slurry. A honeycomb structure (90 mm diameter and 75 mm length) made of a commercially available cordierite base material was immersed in the impregnation liquid and then taken out of the liquid. Compressed air was blown against the honeycomb structure to remove excessive liquid therefrom. After drying at 120°C , it was heat-treated at 500°C for 1 h.

This procedure was repeated and finally it was calcined at 1000°C for 2 h. The thus treated honeycomb structure had 18.7 wt. % of a composite oxide layer. The specific surface area of the surface layer was 13.5 m²/g. The honeycomb 5 structure was then immersed in an aqueous mixture of chloroplatinic acid and rhodium chloride, dried at 120°C and reduced in hydrogen stream at 600°C. The catalyst contained 1.5 wt. % of platinum and 0.4 wt. % of rhodium.

The thus obtained catalyst was used for oxidation of an 10 automobile exhaust gas. The catalyst was used as a catalytic converter for an ordinary automobile engine (1.8 l class). After 10,000 km travelling test, the results were 1.0 g/km of CO and 0.19 g/km of HC (in 10-mode). It is understood from these results that the heat-resistant catalyst of the 15 present invention can be used for the treatment of an exhaust gas from an internal combustion engine to exhibit its effects stably in the high-temperature reaction.

Example 3

In this example, the heat-resistant catalyst of the 20 present invention was used in a high-temperature steam reforming reaction of hydrocarbons.

100 g of the support of the present invention obtained in Example 1 was impregnated with an aqueous nickel nitrate solution, dried at 120°C and calcined at 900°C for 2 h. The 25 catalyst thus obtained contained 15 wt. % (as NiO) of nickel.

The catalyst thus obtained was charged in a reaction tube and reduced in H_2 stream at $600^\circ C$ for 2 h. Then, a steam reforming reaction of n-butane was carried out while the inlet and outlet temperatures of the catalyst bed were 5 maintained at 580 to $600^\circ C$ and 850 to $900^\circ C$, respectively, under a pressure of 15 kg/cm^2 . The molar ratio of steam to carbon was 3.0 and space velocity was 3000 h^{-1} . After the continuous test effected for 100 h, n-butane conversion was maintained above 99.9 %. After completion of the reaction, 10 carbon deposit was hardly recognized on the catalyst bed.

The gaseous reaction product comprised H_2 , CO , CO_2 and CH_4 .

The ratio of these components was almost equal to that of an equilibrium composition obtained at the above-mentioned temperature of the catalyst bed outlet.

15 It is apparent from the results of this example that the heat-resistant catalyst of the present invention exhibits excellent effects also in the high-temperature steam reforming reactor.

Example 4

20 In this example, the heat-resistant catalyst of the present invention was used in a high-temperature denitration reaction.

50 g of a powder of the composite oxide (not shaped) prepared in the same manner as in Example 1 was kneaded 25 thoroughly with 500 g (150 g as TiO_2) of a metatitanic acid

slurry by means of a kneader. The mixture was dried at 150°C. pulverized and preliminary calcined at 400°C for 4 h. The specific surface area of the support was 80 m²/g. The resulting powder was shaped into columnar moldings having 3 mm diameter 5 and 3 mm thickness by means of a press molding machine. The moldings were then immersed in an aqueous hydrogen peroxide solution containing ammonium tungstate. After calcining them at 600°C for 2 h, a catalyst containing 5 wt. % of tungsten oxide was obtained.

10 A gas having the following composition was treated at a reaction temperature of 600°C and at a space velocity of 5000h⁻¹ for 100 h.

Composition of reaction gas:

15	NO _x	200 ppm
	NH ₃	200 ppm
	O ₂	3 %
	H ₂ O	10 %
	N ₂	the balance

20 The NO_x removal was 94.8 % in the initial stage and 94.4 % after 100 h. It is apparent from the above-mentioned results that the catalyst of the present invention exhibits excellent effects also in the high-temperature denitration reaction.

Example 5

25 In this example, the catalyst of the present invention was used in a methanization reaction of CO.

Each of the two supports obtained in Example 1 was impregnated with nickel nitrate, calcined at 500°C, then impregnated with ruthenium chloride and calcined at 1000°C for 2 hours to obtain a catalyst. This catalyst contained 5 30 % of NiO and 3 % of Ru. The catalyst was charged in a reaction tube. A gas comprising 5 % of CO, 17 % of H₂ and the balance of N₂ was introduced therein at a space velocity of 100,000 h⁻¹. The methanation reaction was carried out at 350°C. The conversion of CO by the methanation reaction 10 in this example was 15-folds of that obtained by using the catalyst of Comparative Example 1. It will be understood from these results that the catalyst of the present invention is quite effective not only for the high-temperature reactions but also for the relatively low-temperature reaction.

15 Example 6

In this example, the effects of the catalyst in a dehydrogenation reaction of methanol were examined.

Each of the two carriers obtained in Example 1 was impregnated with a solution of copper nitrate or zinc nitrate. 20 They were dried and then calcined at 1000°C for 2 hours. The Cu and Zn contents of the carriers were 20 wt. % and 10 wt. %, respectively. The resulting carriers were each charged in a reaction tube and the temperature was elevated to 800°C. Methanol was introduced therein to effect the 25 dehydrogenation reaction and to obtain formalin. Methanol

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conversion was at least 98 % and formaldehyde selectivity was 5-folds of that obtained in a conventional process.

Example 7

500g of aluminum nitrate and 30.7g of neodymium nitrate 5 were dissolved in 5 l of distilled water. To the solution was added 3N aqueous ammonia under stirring to adjust a pH value thereof to 8 so as to effect coprecipitation.

The resulting precipitate was recovered by decantation and rinsed with distilled water, and then the precipitate was 10 filtered. The precipitate obtained was dried at 150°C for one day. The dried precipitate was crushed and pre-calcined at 500°C for 2 hours; 0.5% by weight of graphite powder was added to the crushed calcining.

The powder mixture was shaped into a column of 3 mm 15 diameter and of 3 mm length by means of a press molding machine.

The composition of the molding was 5 mol% of Nd_2O_3 and 95 mol% of Al_2O_3 . The molding was then calcined at 1200°C for 2 hours. The resulting support A had a specific surface 20 area and a structure shown in Table 3.

Example 8

Various supports having different molar ratios of Al_2O_3 and Nd_2O_3 were prepared in the same manner as in Example 7. The specific surface areas and structures of the composite 25 oxides obtained are shown in Table 3 wherein support B has

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a composition of 2 mol% of Nd_2O_3 -98 mol% of Al_2O_3 ; support C 10 mol% of Nd_2O_3 -90 mol% of Al_2O_3 and support D 20 mol% of Nd_2O_3 -80 mol% of Al_2O_3 .

Table 3

Support	Surface Area (m^2/g)	Structural form
A	23.4	Mixture of $\text{Nd}-\beta\text{-Al}_2\text{O}_3$ and the precursor
B	21.5	Mixed phase of $\text{Nd}-\beta\text{-Al}_2\text{O}_3$, the precursor and $\alpha\text{-Al}_2\text{O}_3$
C	19.3	ditto
D	14.2	ditto

10

Example 9

500g of aluminum nitrate and 30.5g of praseodymium were dissolved in distilled water. Supports having compositions shown in Table 4 were prepared in the same manner as in
15 Example 7. The surface areas and structural forms of the resulting supports were examined and are shown in Table 4, wherein support E has a composition of 2 mol% of Pr_2O_3 and 98 mol% of Al_2O_3 ; support F 5 mol% of Pr_2O_3 and 95 mol% of Al_2O_3 ; support G 10 mol% of Pr_2O_3 and 90 mol% of Al_2O_3 ; and
20 support H 20 mol% of Pr_2O_3 and 80 mol% of Al_2O_3 .

Table 4

Support	Surface Area (m^2/g)	Structural form
E	20.1	$\text{Pr}-\beta\text{-Al}_2\text{O}_3$
F	22.9	Mixed phase of $\text{Pr}-\beta\text{-Al}_2\text{O}_3$, the precursor and $\alpha\text{-Al}_2\text{O}_3$
G	17.5	ditto
H	13.0	ditto

25

Example 10

500g of aluminum nitrate, 18.6g of neodymium nitrate and 18.5g of praseodymium nitrate were dissolved in distilled water.

5 A support was prepared in the same manner as in Example 7. The support has a composition of 3 mol% of Nd_2O_3 , 3 mol% of Pr_2O_3 and 94 mol% of Al_2O_3 ; a surface area of $23.0 \text{ m}^2/\text{g}$; and a structural form of a mixed phase of a phase resemble to Nd- β -alumina and Pr- β -alumina and $\alpha\text{-Al}_2\text{O}_3$.

10 Example 11

500g of alumina sol (alumina content : 9.8wt%) and 12.3g of neodymium carbonate were kneaded with a kneader for 2 hours; then, the mixture was dried at 150°C for one day.

The dried mixture was crushed to under 60 mesh; the 15 resulting powder was pre-calcined at 500°C for 2 h, mixed with 0.5% by weight of graphite powder, and was molded into pellets each having a diameter of 3 mm and a length of 3 mm.

The composition of the pellets was 4 mol% of Nd_2O_3 and 96 mol% of Al_2O_3 . The pellets were calcined at 1000°C 2 hours or 1200°C for 2 hours. The resulting supports calcined at 1000°C had a specific surface area of $96.5 \text{ m}^2/\text{g}$ and the supports calcined at 1200°C had a specific surface area of $21.6 \text{ m}^2/\text{g}$.

Pd-Catalysts prepared in the same manner as in Example 25 1 using the supports obtained in Examples 7-10 exhibited good

durability at temperatures as high as 800 to 1400°C.

Since the catalysts of the present invention have high specific surface areas, they can be used for chemical reactions at relatively low temperatures, as well as at high 5 temperatures.

Example 11

The support prepared in Example 1 was impregnated with a solution of ammonium molybdate and nickel nitrate, and was dried. Thereafter, the impregnated support was calcined at 10 500°C for 5 hours. The composition of the catalyst obtained was 15% by weight of MoO_3 and .5% by weight of NiO , and the balance being the support.

40ml catalyst was filled in a reactor having an inner diameter of 15mm. Hydrogen gas was flown in the reactor at 15 a rate of about 1l/min. at 450°C for 5 hours to reduce the catalyst.

Then, hydrogen gas was supplied to the reactor at a rate of 300ml/min and n-hexane containing 100 ppm of thiophene was supplied at a rate of 100ml/h to effect desulfurization 20 reaction by hydrogenation. The content of sulfur in the effluent gas was determined by gas chromatograph. Even after the 100 hours test, the sulfur content was less than 0.1 ppm.

Example 12

The support prepared in Example 1 was impregnated with 25 a solution of chloroplatinic acid and was dried. The impregnated

support was calcined at 900°C for 2 hours. The content of platinum of the catalyst was 1% by weight.

5cc of the catalyst was filled in a reactor to which air containing 100ppm of methylethyl ketone, toluene and 5 formaldehyde was supplied. The catalytic reaction was conducted at 500°C. The content of the odorous compounds in the effluent gas was only 0.4 ppm of methylethyl ketone, 0.3 ppm of toluene and 0.8 ppm of formaldehyde.

Example 13

10 The powdered support prepared in Example 1 was thoroughly mixed with a slurry of β -stannic acid and the mixture was dried. The mixture was calcined at 500°C for 3 hours. 1 g of the catalyst was added to 20 g of heavy oil. The oil was charged in an autoclave and subjected to a reaction at 400°C 15 under a pressure of 100 kg/cm² in the stream of hydrogen gas for 30 min. After the reaction, the product was subjected to distillation under a reduced pressure. The composition of the product was as follows:

	Boiling point (°C)	Composition (% by weight)
20	~ 200	9
	200 ~ 350	39
	350 ~ 550	37
	residue	15

Example 14

25 The support prepared in Example 1 was impregnated with

a solution of copper chlorate and dried. The support was calcined at 500°C for 2 hours. The composition of the catalyst was 20 % by weight of Cu₂O and the balance being 80 % by weight of the support.

5 An oxidation reaction of propylene was conducted using 20 ml of the catalyst. The reactive gas used was 25% by volume of C₃H₆, 10 % by volume of O₂ and the balance being N₂. The reaction temperature was 450°C. The analysis of the product gas showed that the conversion rate of C₃H₆ to 10 acrolein was 98 % and the selection ratio to acrolein was 88 %.

Example 15

The support prepared in Example 1 was impregnated with a solution of cobalt nitrate and iron nitrate (III). The 15 resulting impregnate was dried and calcined at 800°C for 5 hours. The composition of the catalyst was 12% by weight of CoO, 8% by weight of Fe₂O₃, and the balance being the support.

40 ml of the catalyst was contacted with gas consisting of 40 % by volume of CO and 60 % by volume of H₂ at 300°C 20 under a pressure of 50 kg/cm². The conversion rate of [CO + H₂] to organic compounds was 88 %. The selection ratios of the gas were 48 % for C₁~C₅, 21% for gasoline 12 % for oxygen-containing compounds, and 29 % for heavy oil.

Example 16

25 The support prepared in Example 1 was impregnated with

copper nitrate, and zinc nitrate. The support was dried and calcined at 500°C for 2 hours. The catalyst was contacted with a gas consisting of 75 % by volume of H₂ and 25 % by volume of CO at a temperature of 300°C under a pressure of 5 100 kg/cm². The analysis of the product gas showed that the conversion rate of [H₂ + CO] to methanol was 90 % and the selection ratio for methanol was 92 %.

Example 17

The support prepared in Example 1 was impregnated with 10 nickel nitrate and dried. The support was calcined at 500°C for 2 hours to obtain a catalyst having a composition of 15% by weight of NiO and the balance being the support.

The catalyst was contacted with n-butane at 100°C so as to effect isomerization reaction to iso-butane. The conversion rate of n-butane to iso-butane was 69 %.

Example 18

The support prepared in Example 1 was impregnated with cobalt nitrate and dried. The support was then calcined at 600°C for 2 hours. The catalyst was used for cracking of 20 heavy oil at 450°C to produce a product containing about 40% by weight of gasoline distillate without deposition of carbon on the catalyst.

Example 19

The support prepared in Example 1 was impregnated with 25 a solution of iron chloride, potassium chloride and copper

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chloride and dried.

The catalyst was calcined at 700°C for 2 hours to have a composition of 20 % by weight of Fe_3O_4 , 2 % by weight of K_2O , 2 % by weight of CuO , and the balance being the support.

5 The catalyst was then contacted with a gas consisting of 75 % by volume of H_2 and 25 % by volume of N_2 at 550°C under a pressure of 250 kg/cm². The conversion rate of $[\text{H}_2 + \text{N}_2]$ to NH_3 was 95%.

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CLAIMS

1. A high temperature stable catalyst, which comprises a support and a catalytically active component supported on said support, wherein at least the part of said support
- 5 that predominantly supports said active component comprises a composite oxide of aluminium and at least one member selected from the group of lanthanum, neodymium, praseodymium and mixtures thereof, said composite oxide having a specific surface area of at least 10 m²/g, where said composite oxide
- 10 is substantially a mixture of L- β -alumina and its precursor that is convertible to L- β -alumina when heated to an elevated temperature above 1000°C within 2 hours or substantially the precursor.
2. A high temperature stable catalyst according to claim 1, 15 wherein the composite oxide has a composition of 1 to 20 molar % of the oxide of lanthanum, neodymium and praseodymium and the balance being alumina.

3. A high temperature stable catalyst, which comprises a support and a catalytically active component supported on said support, wherein at least the part of said support that predominantly supports said active component comprises.

5 a composite oxide of aluminium and at least one member selected from the group of lanthanum, neodymium, praseodymium and mixtures thereof, said composite oxide having a specific surface area of at least $10 \text{ m}^2/\text{g}$, where said composite oxide contains less than 1% by weight of chromium, strontium and

10 cerium, has a composition of 1 to 20 molar % of the oxide of lanthanum, neodymium and praseodymium and the balance being alumina, the composite oxide being substantially a mixture of γ -alumina and its precursor or the precursor.

4. A high temperature stable catalyst, which comprises a support and a catalytically active component supported on said support, wherein at least the part of said support that predominantly supports said active component comprises

25 a composite oxide of aluminium and at least one member

selected from the group of lanthanum, neodymium, praseodymium and mixtures thereof, said composite oxide having a specific surface area of at least 10 m²/g and having a structural form other than α -, γ -, δ -, η -, κ -, χ -, σ and ζ -forms, where said

5 composite oxide contains less than 1% by weight of chromium, strontium and cerium, and is a mixture of L- α -alumina and its precursor that is convertible to L- β -alumina when heated to an elevated temperature above 1000°C within 2 hours, or the precursor, wherein the composite oxide has a composition of

10 1 to 20 molar % of the oxide of lanthanum, neodymium and praseodymium and the balance being alumina.

5. A high temperature stable catalyst, which comprises a

20 support and a catalytically active component supported on said support, wherein at least the part of said support that predominantly supports said active component comprises a composite oxide of aluminium and at least one member selected from the group of lanthanum, neodymium, praseodymium

25 and mixtures thereof, said composite oxide having a specific

surface area of at least 10 m²/g, where said composite oxide contains less than 1% by weight of chromium, strontium and cerium, and is substantially L- β -alumina and its precursor that is convertible to L- β -alumina when heated to an elevated 5 temperature above 1000°C within 2 hours, wherein the composite oxide has a composition of 1 to 20 molar % of the oxide of lanthanum, neodymium and praseodymium and the balance being alumina.

6 . A high temperature stable catalyst according to any one of claims 1 to 5 10 wherein the composite oxide has a composition of 3 to 10 molar % of the oxide of lanthanum, neodymium and praseodymium and the balance being alumina.

7 . A high temperature stable catalyst according to any one of claims 1 to 7 15 wherein the composite oxide has a specific surface area of 20 to 100 m²/g.

8 . A high temperature stable catalyst according to any one of claims 1 to 7 wherein the shape of the support is a honeycomb structure.

9 . A high temperature stable catalyst according to any one of claims 1 to 8 20 wherein the support comprises the part for supporting the active component and a substrate for carrying the support.

10 . A high temperature stable catalyst according to claim 9,, wherein the substrate is a member selected from a metallic plate, metallic mesh, and foamed metal.

11 . A high temperature stable catalyst according to any one of claims 1 to 10, 25 wherein the surface of the support is coated with the composite

oxide on which said active component is supported.

12 . A high temperature stable catalyst according to any one of claims 1 to 11, wherein the active component is a member selected from the group consisting of Group VIII elements of the Periodic

5 Table, manganese, chromium, zirconium, rare earth elements, tin, zinc, copper, magnesium, barium, strontium, vanadium, tungsten, molybdenum, titanium, gallium, indium, lead, bismuth, antimony, chromium, silver, and calcium.

13 . A process for preparing a high temperature stable
10 catalyst, which comprises the steps of:

effecting coprecipitation of an aluminum salt and a salt of lanthanum, praseodymium and/or neodymium from an aqueous solution of the salts by adding an alkali to the solution;

15 separating the resulting precipitate;

shaping the precipitate; and

heating to a temperature higher than 1000°C the shaped precipitate to convert it into a composite oxide of aluminium and lanthanum, neodymium and/or praseodymium, whereby said

20 composite oxide has a specific surface area of at least 10 m²/g and is substantially a mixture of L-β-alumina and its precursor that is convertible to L-β-alumina when heated to an elevated temperature above 1000°C preferably within 2 hours or substantially the precursor.

25 15. A process for conducting a catalytic chemical reaction,

which comprises contacting a reactive component with a catalyst comprising a support and a catalytically active component supported on said support, wherein at least the part of said support that predominantly supports said active

5 component comprises a composite oxide of aluminium and at least one member selected from the group of lanthanum, neodymium, praseodymium and mixtures thereof, said composite oxide having a specific surface area of at least 10 m²/g, where said composite oxide contains less than 1% by weight

10 of chromium, strontium and cerium, and is substantially a mixture of L- β -alumina and its precursor that is convertible to L- β -alumina when heat to an elevated temperature above 1000°C within 2 hours or substantially the precursor.

15. A process for conducting a catalytic chemical reaction

15 according to claim 14 wherein the composite oxide has a composition of 1 to 20 molar % of the oxide of lanthanum, neodymium and/or praseodymium and the balance being alumina.

16. A process for conducting a catalytic chemical reaction according to claim 15, wherein the composite oxide has a composition of 3 to 10 molar % of the oxide of lanthanum, neodymium and/or praseodymium and the balance being alumina.

17. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 16 wherein the composite oxide has a specific surface area of 20 to 100 m^2/g .

18. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 17 wherein the catalyst is according to any one of claims 1 to 12.

19. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 18, wherein the active component is at least one member selected from the group consisting of Group VIII elements of the Periodic Table, manganese, chromium, zirconium, rare earth elements, tin, zinc, copper, magnesium, barium, strontium and calcium.

20. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein the catalyst is contacted with a fluid fuel and oxidant for catalytic combustion.

21. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein said catalyst is contacted with at least one of hydrogen, carbon monoxide, alcohols, hydrocarbons and mixtures thereof.

22. A process for conducting a catalytic chemical reaction according to claim 21 wherein said hydrocarbon is methane and said catalytically active component is at least one of

the Group VIII elements of Periodic Table.

23. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 18 wherein the catalyst is contacted with an exhaust gas from an internal combustion engine and oxygen

5 to oxidize carbon monoxide and hydrocarbons in said exhaust gas and to reduce nitrogen oxides in said exhaust gas, wherein the catalytically active component is a member selected from the group consisting of the Group VIII elements, manganese, rare earth metal, chromium, vanadium, tin, zirconium,

10 magnesium, calcium and/or strontium.

24. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein said catalyst is contacted with a stream of a mixture of hydrocarbons and steam at a temperature of 300 to 1200°C to form a gas comprising

15 hydrogen and carbon monoxide.

25. A process for conducting a catalytic chemical reaction according to claim 19 or claim 23 wherein said active component is at least one Group VIII element of the Periodic Table.

26. A process for conducting a catalytic chemical reaction

20 according to any one of claims 14 to 19 wherein said catalyst is contacted with an exhaust gas containing nitrogen oxide and also with ammonia at a temperature of 150°C to 1000°C to reduce the nitrogen oxide.

27. A process for conducting a catalytic chemical reaction

25 according to claim 26, wherein said active component is at

least one of tungsten, vanadium, titanium, tin, cerium, iron, nickel and cobalt.

28. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein said catalyst is contacted with hydrocarbons at a temperature ranging from 500°C to 1000°C to effect the dehydrogenation.

29. A process for conducting a catalytic chemical reaction according to claim 21, wherein said catalyst is contacted with methanol at a temperature of 800°C to 1000°C.

10 30. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein the active component is a member selected from the group consisting of molybdenum, tungsten, nickel and cobalt, and the catalyst is contacted with hydrocarbon oil containing a sulfur compound at 250°C to 15 500°C under 1 to 100 kg/cm² in the presence of hydrogen so as to effect desulfurization of the oil.

31. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein the active component is at least one member selected from the group consisting of Group 20 VIII elements, manganese, titanium, zinc, copper, rare earth metal elements, tungsten, chromium, vanadium, and zirconium, and the catalyst is contacted with a gas containing an odorous organic compound and oxygen at a temperature of 100 to 1500°C so as to remove the odorous compound.

25 32. A process for conducting a catalytic chemical reaction

according to any one of claims 14 to 19 wherein the active component is at least one member selected from the group consisting of

Group VIII elements titanium, zirconium, vanadium, molybdenum, tungsten, manganese, copper, zinc, gallium,

5 indium, tin, lead, bismuth and antimony, and the catalyst is contacted with heavy oil, asphalt or coal in the presence of hydrogen at a temperature of 350 to 800°C under a pressure of 1 to 500 kg/cm² so as to produce light oil.

33. A process for conducting a catalytic chemical reaction

10 according to any one of claims 14 to 19 wherein the active component is at least one member selected from the group consisting of Group VIII elements, manganese, chromium, zirconium, rare earth elements, tin, zinc, copper, silver, magnesium, barium, strontium and calcium, and the catalyst is contacted with a

15 gas containing an organic substance at a temperature of 1500°C or below.

34. A process for conducting a catalytic chemical reaction according to claim 21 wherein the catalyst is contacted with a gas containing carbon monoxide and hydrogen at a temperature

20 of 1000°C or below under a pressure of 1 to 200 kg/cm².

35. A process for conducting a catalytic chemical reaction according to claim 21 wherein the catalyst is contacted with carbon monoxide and hydrogen at a temperature of 600°C or below under a pressure of 1 to 200 kg/cm² so as to produce methanol.

25 36. A process for conducting a catalytic chemical reacting

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according to claim 21, wherein the catalyst is contacted with a hydrocarbon at a temperature of 700°C or below so as to effect isomerization of the hydrocarbon.

37. A process for conducting a catalytic chemical reaction
5 according to claim 21, wherein the catalyst is contacted with gaseous hydrocarbons at a temperature of 1000°C or below so as to effect cracking of the hydrocarbons.

38. A process for conducting a catalytic chemical reaction according to any one of claims 14 to 19 wherein the catalyst is contacted with
10 an organic compound and/or nitrogen in the presence of hydrogen at a temperature of 800°C or below under a pressure of 500 kg/cm² or below.

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FIG. 1

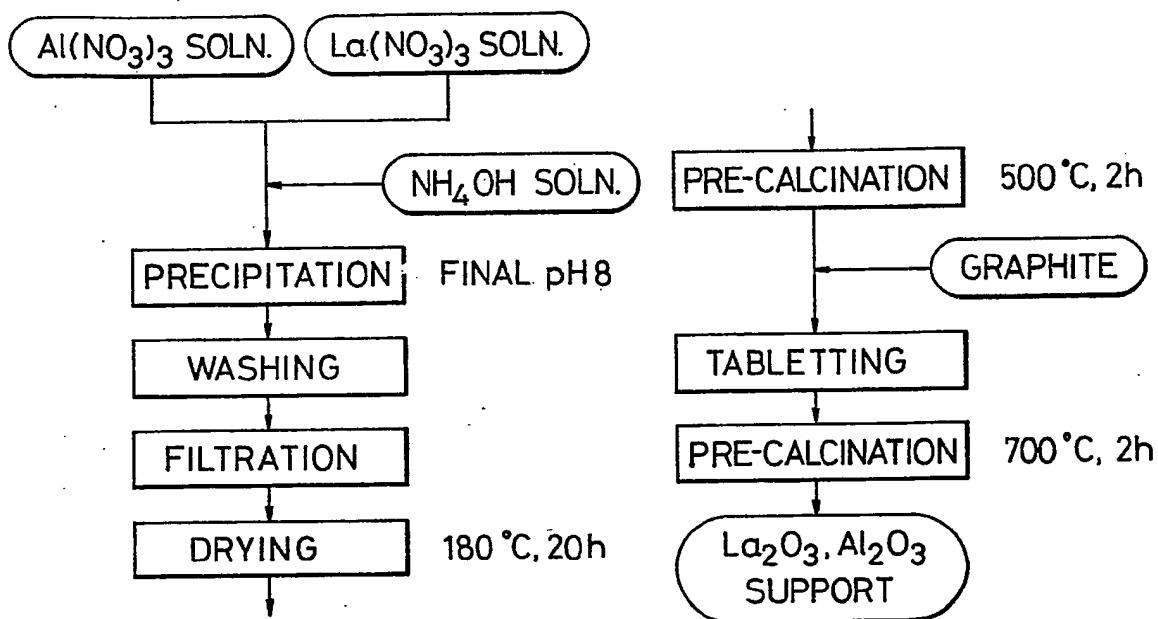
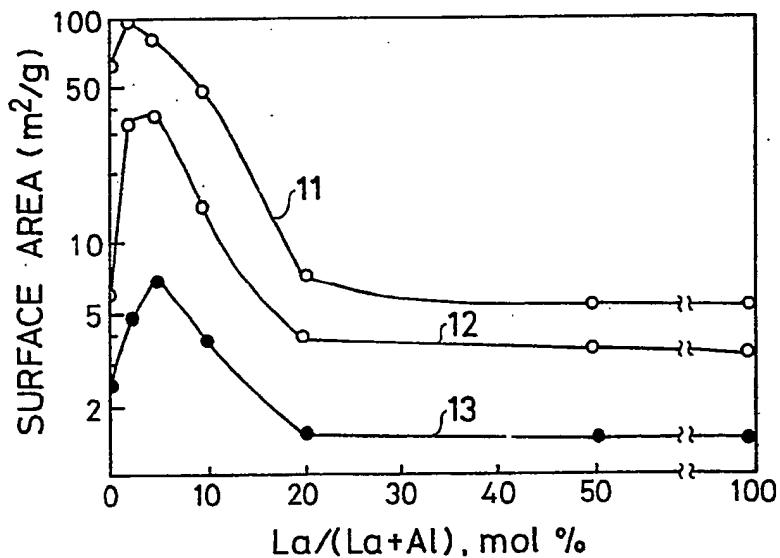


FIG. 2



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FIG. 3a La/Al
0/100

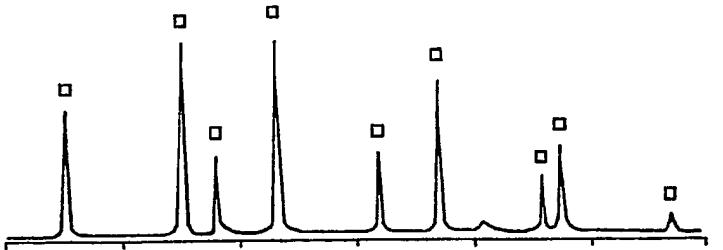


FIG. 3b 5/95

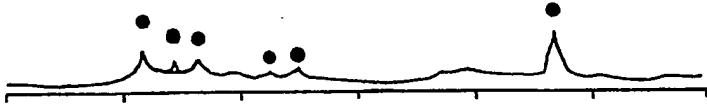


FIG. 3c 10/90

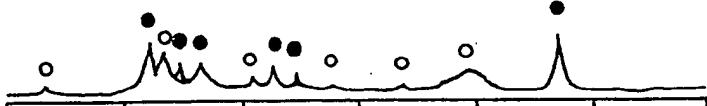


FIG. 3d 50/50

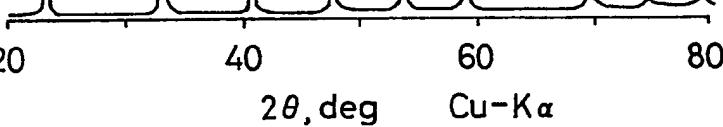
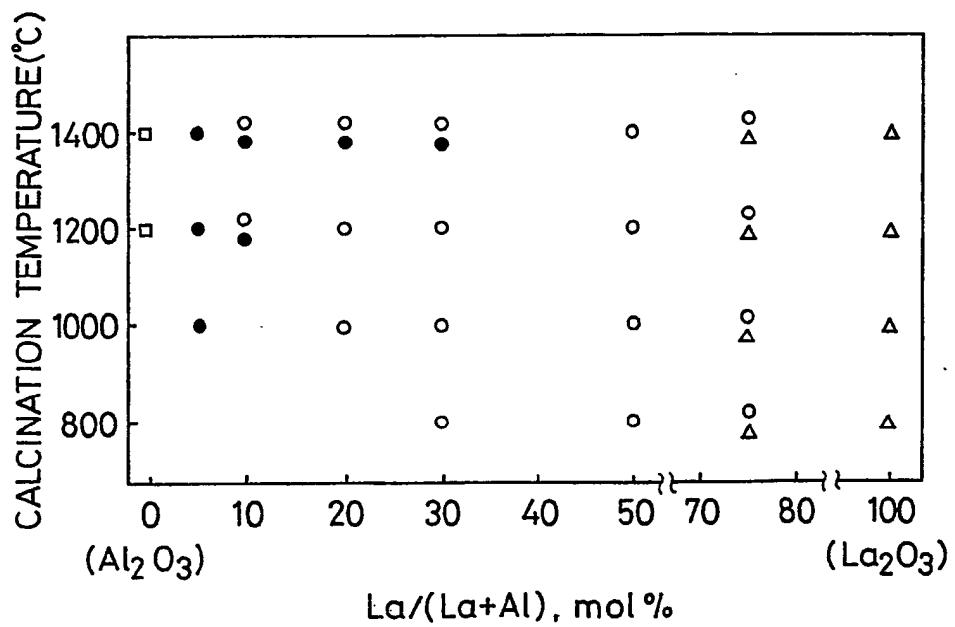


FIG. 4



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FIG. 5

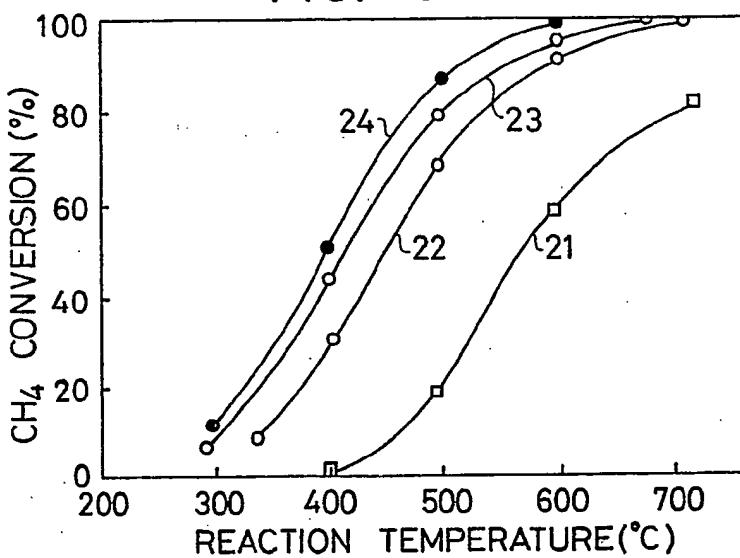


FIG. 6

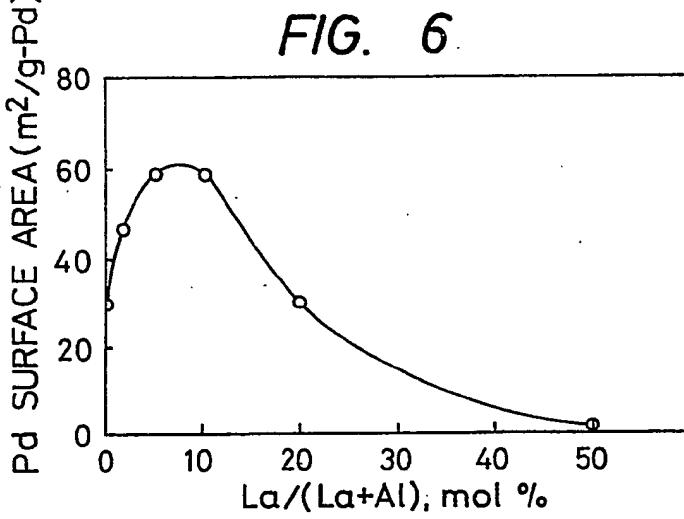
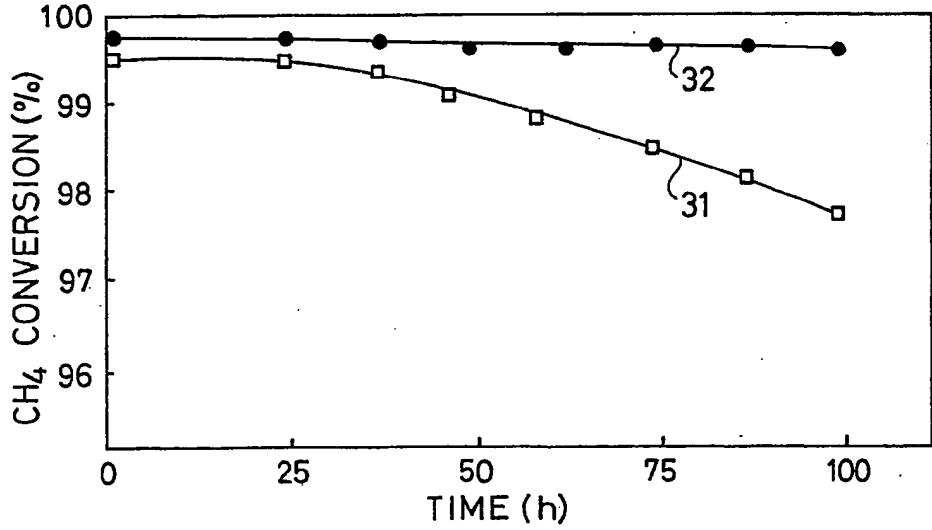


FIG. 7





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C 10 G 49/02, C 07 C 29/15
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㉘ High temperature stable catalyst, process for preparing same and process for conducting chemical reaction using same.

㉙ A high temperature-stable catalyst comprising an alumina base support and a catalytically active component supported on the support.

The support comprises a composite oxide of aluminum and lanthanum and/or neodymium and/or praseodymium, said composite oxide having a specific surface area of at least 10 m²/g and a structural form of an amorphous state or a structure resembling L-beta-alumina, or a precursor which can be converted into L-beta-alumina when heated to a temperature above 1000° C for 2 hours.

The composite oxide is substantially free from such ingredients as accelerate grain growth of alumina, for example Cr, Sr or Ce.

The catalyst is used for conducting chemical reactions such as steam reforming, desulfurization of heavy oil, cracking of hydrocarbons.

EP 0 130 835 A3



EP 84 30 4514

DOCUMENTS CONSIDERED TO BE RELEVANT									
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl 4)						
A	FR-A-2 257 335 (RHONE-PROGIL)		B 01 J 23/00 B 01 J 23/10 B 01 J 32/00 C 01 B 3/40 C 07 C 5/32 C 10 G 49/02 C 07 C 29/15 C 07 C 5/22 C 10 G 11/04 F 23 C 11/00						
	DE-A-2 500 548 (RHONE-POULENC)								

	FR-A-2 253 560 (ENGELHARD MINERALS) * Pages 5-6; pages 25-26; example 24 *								
	FR-A-2 171 160 (ETHYL CORPORATION)								

			TECHNICAL FIELDS SEARCHED (Int. Cl 4)						
			B 01 J 23/00						
<p>The present search report has been drawn up for all claims</p> <table border="1"> <tr> <td>Place of search</td> <td>Date of completion of the search</td> <td>Examiner</td> </tr> <tr> <td>THE HAGUE</td> <td>22-12-1986</td> <td>DEVISME F.R.</td> </tr> </table> <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>				Place of search	Date of completion of the search	Examiner	THE HAGUE	22-12-1986	DEVISME F.R.
Place of search	Date of completion of the search	Examiner							
THE HAGUE	22-12-1986	DEVISME F.R.							